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Abstract

Treatment of a single crystal Si wafer (n- or p-type, 100 face) having a thin surface SiO_x layer with $\text{Cl}_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, I, yields the Si-confined complex $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. Coverage of about a monolayer is typically achieved. Near-UV irradiation of the Si-confined tricarbonyl in $\text{L} = \text{PPh}_2(n\text{-octyl})$ gives the surface-confined substitution product $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$. The identities of the Si-confined complexes were determined by comparison of their IR CO stretching frequencies with those of $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, and of the corresponding high surface area SiO_2 -confined species, $[\text{SiO}_2]\text{-O-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$ ($\text{L} = \text{CO}, \text{PPh}_2(n\text{-octyl})$). Treatment of a Au-coated Si wafer with $\text{HS}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, II, yields about a monolayer of the Au-confined complex $[\text{Au}]\text{-S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. Near-UV irradiation of the Au-confined tricarbonyl in the presence of $\text{L} = \text{PPh}_2(n\text{-octyl})$ yields the surface-confined substitution product $[\text{Au}]\text{-S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$. The photochemistries of surface-confined I and II differ from the photochemistries of the corresponding solution species. No surface-confined disubstituted species $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ or $[\text{Au}]\text{-S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ are formed, although $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})\text{L}_2$, $\text{R} = -\text{Si}(\text{CH}_3)_3$ or $-(\text{CH}_2)_{11}\text{SH}$, form readily upon irradiation of $(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$ in solutions containing $\text{PPh}_2(n\text{-octyl})$. In addition, even the formation of monosubstitution products is more difficult on

a surface than in solution. The difficulty is manifested by the need for high entering ligand concentrations and the inability to achieve significant chemical yields of $[\text{Si}]\text{-O-Si-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$ or $[\text{Au}]\text{-S(CH}_2\text{)}_{11}\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$ with a wide range of L. This and the absence of multiple substitution products is rationalized by invoking interaction of the surface-confined molecule with the surface. Patterning of the surface of a Si wafer modified with I or of Au modified with II is readily accomplished, since photosubstitution occurs only on irradiated portions of the surface.

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Patterned Functionalization of Gold and Single Crystal Silicon
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 $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$

by

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Silicon via Photochemical Reaction of Surface-Confined
Derivatives of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$**

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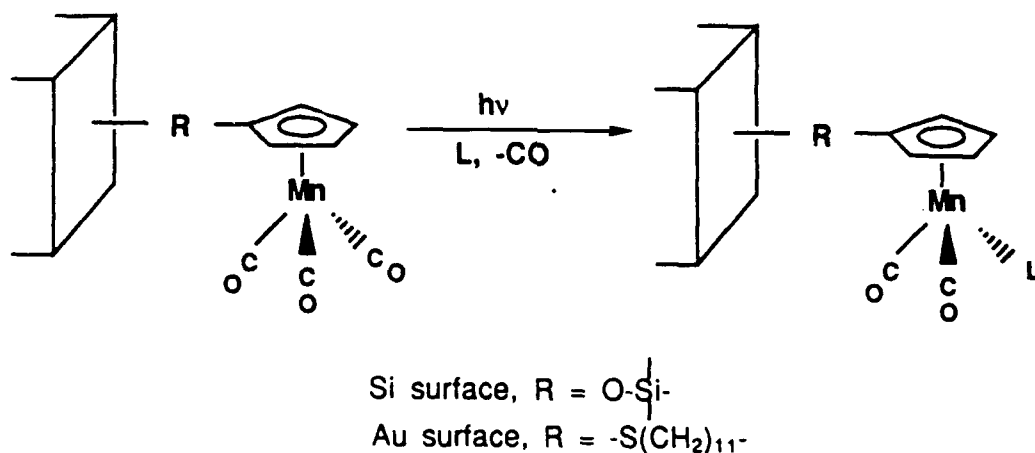
Abstract

Treatment of a single crystal Si wafer (n- or p-type, 100 face) having a thin surface SiO_x layer with $\text{Cl}_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, I, yields the Si-confined complex $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. Coverage of about a monolayer is typically achieved. Near-UV irradiation of the Si-confined tricarbonyl in $\text{L} = \text{PPh}_2(n\text{-octyl})$ gives the surface-confined substitution product $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$. The identities of the Si-confined complexes were determined by comparison of their IR CO stretching frequencies with those of $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, and of the corresponding high surface area SiO_2 -confined species, $[\text{SiO}_2]\text{-O-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$ ($\text{L} = \text{CO}, \text{PPh}_2(n\text{-octyl})$). Treatment of a Au-coated Si wafer with $\text{HS}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, II, yields about a monolayer of the Au-confined complex $[\text{Au}]\text{-S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. Near-UV irradiation of the Au-confined tricarbonyl in the presence of $\text{L} = \text{PPh}_2(n\text{-octyl})$ yields the surface-confined substitution product $[\text{Au}]\text{-S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$. The photochemistries of surface-confined I and II differ from the photochemistries of the corresponding solution species. No surface-confined disubstituted species $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ or $[\text{Au}]\text{-S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ are formed, although $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})\text{L}_2$, $\text{R} = \text{-Si}(\text{CH}_3)_3$ or $\text{-(CH}_2)_{11}\text{SH}$, form readily upon irradiation of $(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$ in solutions containing $\text{PPh}_2(n\text{-octyl})$. In addition, even the formation of monosubstitution products is more difficult on

a surface than in solution. The difficulty is manifested by the need for high entering ligand concentrations and the inability to achieve significant chemical yields of $[\text{Si}]\text{-O-Si-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$ or $[\text{Au}]\text{-S(CH}_2\text{)}_{11}\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$ with a wide range of L. This and the absence of multiple substitution products is rationalized by invoking interaction of the surface-confined molecule with the surface. Patterning of the surface of a Si wafer modified with I or of Au modified with II is readily accomplished, since photosubstitution occurs only on irradiated portions of the surface.

Introduction

We wish to report photochemical patterning of the SiO_x surface of single crystal Si (100 face) modified with $\text{Cl}_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, I, and of Au surfaces modified with $\text{HS}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, II, by selective photosubstitution of $\text{L} = \text{PPh}_2(n\text{-octyl})$ for CO. This process is shown in Scheme I.



Scheme I. Photochemical functionalization of the surface of single crystal Si modified with I or Au modified with II.

Photoinduced ligand substitution processes have been observed for several metal carbonyl complexes covalently bound or adsorbed to solid supports, such as SiO_2 powders;¹ porous Vycor glass;² chloromethylated polystyrene;^{1e} single crystal Rh,³ Al_2O_3 ,⁴ Ag,⁴ and Si.^{4,5} For a variety of mononuclear metal carbonyls CO loss occurs as the primary photoprocess, and the extruded ligand can be replaced by another $2e^-$ donor, L.

Our aim is to demonstrate that a flat surface modified with an appropriate metal carbonyl can be photochemically patterned with respect to the functional group present in the incoming ligand, L. I and II were considered ideal for the preparation of surfaces to be photochemically patterned because $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ is reported to be especially inert towards thermal CO substitution⁶ but undergoes efficient photoinduced CO substitution reactions with a wide variety of incoming ligands.⁷

It has been shown that Cl_3SiR reagents yield about one monolayer of the functional group R attached to a Si/SiO_x surface.⁸ The formation of monolayer films by adsorption of organic thiols onto Au is also a well-documented process.⁹

Experimental Section

Materials. Tetrahydrofuran (THF), hexane, and toluene were freshly distilled from CaH_2 under N_2 . CH_2Cl_2 was distilled from P_2O_5 under Ar. Methylcyclohexane (J.T. Baker, Photrex) was used as received.

MeOH was distilled from $\text{Mg}(\text{OCH}_3)_2$ under Ar. Pyridine was distilled from KOH under Ar. $(\text{CH}_3)_2\text{SiCl}_2$ (Silar) and SiCl_4 (Alfa) were distilled from quinoline and stored over Mg turnings. Et_3SiH (Petrarch), $\text{CF}_3\text{CO}_2\text{H}$ (Aldrich) and SOCl_2 (Fluka) were used as received.

$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (Strem or Aldrich), 11-bromo-undecanoic acid (Aldrich), AlCl_3 (Mallinkrodt), and $\text{NaSH}\cdot x\text{H}_2\text{O}$ (Aldrich) were used as received.

$(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ was synthesized according to a literature procedure.¹⁰ $\text{PPh}_2(n\text{-octyl})$ was prepared according to a slightly modified literature procedure.¹¹

Silica gel for column chromatography was EM Science Kieselgel 60, 230-400 mesh. High surface area SiO_2 (400 m^2/g , Alfa) was dried for 48h at 200 $^\circ\text{C}$ under 5×10^{-3} Torr vacuum. Substrates for the adsorption of thiols were single crystal Si wafers (Monsanto, 100 face, n-type) cut into ~ 2 cm^2 pieces and coated with ~ 100 Å of Au by sputtering. The Au-coated wafer pieces were stored in Fluoroware trays before use.

All manipulations of air sensitive compounds were carried out on a conventional Schlenk line under Ar or in a Vacuum Atmospheres dry box under Ar.

(CH₃)₃Si-(η⁵-C₅H₄)Mn(CO)₂PPh₂(*n*-octyl). An alkane solution containing ~20 mM (CH₃)₃Si-(η⁵-C₅H₄)Mn(CO)₃ and excess L = PPh₂(*n*-octyl) was irradiated at 25 °C with two blacklight bulbs (output at ~355 nm) until significant conversion of the tricarbonyl to the dicarbonyl phosphine was achieved, as determined by IR. The disubstituted product forms rapidly once the dicarbonyl phosphine is present in solution so care was taken to stop the irradiation prior to extensive formation of secondary photoproducts. The reaction mixture was chromatographed on silica gel with hexane as the eluant. (CH₃)₃Si-(η⁵-C₅H₄)Mn(CO)₃ eluted first, followed by (CH₃)₃Si-(η⁵-C₅H₄)Mn(CO)₂L. The rest of the reaction mixture did not elute with hexane.

CH₃OSi(CH₃)₂-(η⁵-C₅H₄)Mn(CO)₃. To a solution of 1 g (η⁵-C₅H₅)Mn(CO)₃ in 60 ml THF at -42 °C was added 4.1 ml of *n*-BuLi (Alfa, 2.4 M). After 1 h of stirring, the solution now containing Li(η⁵-C₅H₄)Mn(CO)₃ was added to 3 ml of (CH₃)₂SiCl₂ at -42 °C via cannula. The reaction mixture was stirred for 15 min at -42 °C and then slowly warmed to room temperature. Pyridine (2.5 ml) and MeOH (5 ml) were added via syringe to the solution which was stirred for an additional hour. Following removal of solvent, the product was extracted with hexane and purified by vacuum distillation: b.p. 0.00570°C; ¹H NMR (250 MHz, CDCl₃) δ 4.89(s, 2H), 4.84(s, 2H), 3.45(s, 3H), 0.32(s, 6H); IR (hexane) ν_{CO}: 2026, 1946 cm⁻¹.

$[\text{SiO}_2]-\text{O}-\text{Si}(\text{CH}_3)_2-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. Dry, high surface area SiO_2 was stirred in a dry hexane solution containing excess $\text{CH}_3\text{OSi}(\text{CH}_3)_2-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ for 24 h. The concentration of the metal carbonyl in solution was ~ 0.05 M. Following derivatization, the solid was collected in a fritted glass filter and washed liberally with hexane. Elemental analysis for C and Mn (Galbraith Laboratories) established the coverage of the metal carbonyl to be $\sim 4 \times 10^{-11}$ mol/cm², assuming a surface area of 400 m²/g.

$\text{Cl}_3\text{Si}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, I. A solution of $\text{Li}(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ in THF was prepared in the manner described above and added to 4 ml neat SiCl_4 at -42°C via cannula. The product was isolated as described for $\text{CH}_3\text{OSi}(\text{CH}_3)_2-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$: b.p. 0.005 90°C ; ^1H NMR (250 MHz, CDCl_3) δ 5.17(s, 2H), 4.94(s, 2H); IR (hexane) ν_{CO} : 2036, 1960 cm^{-1} . The mass spectrum shows a parent ion region characteristic of a molecule having three Cl atoms, but the molecule is too hydrolytically unstable to obtain a good elemental analysis.

$[\text{Si}]-\text{O}-\text{Si}(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. A single crystal Si wafer (Monsanto, 100 face, n- or p-type) was cut into rectangular pieces $\sim 1 \times 2$ cm and pretreated by etching with HF, followed by immersion in 10 M NaOH for 60 s. The Si wafer pieces were then washed with distilled H_2O and dried in a 125°C oven. Attachment of the metal carbonyl was accomplished by treatment of the Si with a 0.03 M solution of $\text{Cl}_3\text{Si}-(\eta^5-$

$C_5H_4)Mn(CO)_3$ in dry toluene for 48 h. The derivatized Si was washed with THF and allowed to dry in air.

$HS(CH_2)_{11}-(\eta^5-C_5H_4)Mn(CO)_3$, II. A solution containing 13 g 11-bromo-undecanoic acid and 5.2 ml $SOCl_2$ in dry toluene was refluxed for 24 h under Ar. The solvent and excess $SOCl_2$ were removed under reduced pressure, and the acid chloride residue was dissolved along with 10 g $(\eta^5-C_5H_5)Mn(CO)_3$ in 120 ml dry CH_2Cl_2 . After the solution was cooled to 0 °C, 8 g $AlCl_3$ was slowly added. The mixture was stirred at room temperature for 4 h and then hydrolyzed at 0 °C by slow addition of H_2O . The organic layer was separated and dried over $MgSO_4$. The residue obtained upon evaporation of the solvent was chromatographed on silica gel with 2:1 hexane/ CH_2Cl_2 to give purified 11-bromo-undecanoylcyclopentadienylmanganese tricarbonyl as a yellow-orange oil. 1H NMR (250 MHz, $CDCl_3$): δ 5.40 (t, 2H), 4.82 (t, 2H), 3.47 (t, 2H), 2.56 (t, 2H), 1.82 (m, 2H), 1.65 (m, 2H), 1.15-1.5 (m, 12H); IR (MCH) ν_{CO} : 2032, 1959, 1949, 1693 cm^{-1} ; mass spectrum: m/e (relative intensity), 452 (3), 450 (4), 368 (51), 366 (32), 286 (100), 228 (35), 226 (45), 162 (10), 134 (17), 120 (17), 93 (15), 83 (22), 69 (36), 55 (41), 41 (33).

To a solution of 14 g 11-bromo-undecanoylcyclopentadienylmanganese tricarbonyl dissolved in 25 ml CF_3CO_2H were added 11 ml Et_3SiH . The reaction mixture was stirred for 2 days under Ar and then diluted with H_2O and Et_2O . The organic layer was collected and washed with

aqueous NaHCO_3 and H_2O . The residue obtained upon evaporation of solvent was chromatographed on silica gel with hexane to give purified 11-bromo-undecylcyclopentadienylmanganese tricarbonyl, a yellow oil. ^1H NMR (250 MHz, CDCl_3): δ 4.60(m, 4H), 3.47(t, 2H), 2.22(t, 2H), 1.82(m, 2H), 1.15-1.53(m, 16H); IR (hexane) ν_{CO} : 2024, 1942 cm^{-1} ; mass spectrum: m/e (relative intensity), 438 (4), 436 (4), 354 (20), 352 (14), 272 (100), 214 (40), 212 (51), 134 (34), 91 (13), 69 (23), 55 (50), 43 (49).

A solution of 1.1g 11-bromoundecylcyclopentadienyl manganese tricarbonyl in 25 ml absolute ethanol was added dropwise to a solution of 0.31 g $\text{NaSH} \cdot x\text{H}_2\text{O}$ in 30 ml EtOH. The reaction mixture was stirred overnight. Solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and filtered through a pad of silica gel. Evaporation of solvent from the filtrate gave crude product which was chromatographed on silica gel with 4:1 hexane: CH_2Cl_2 to give pure II. ^1H NMR (250 MHz, CDCl_3): δ 4.60(m, 4H), 2.50(q, 2H), 2.22(t, 2H), 1.15-1.6(m, 18H); IR (hexane) ν_{CO} : 2022, 1940 cm^{-1} ; mass spectrum: m/e (relative intensity), 390 (3), 306 (100), 272 (58), 201 (11), 188 (7), 174 (11), 134 (28), 105 (9), 97 (14), 79 (15), 69 (20), 55 (34), 43 (28). Anal. (Galbraith Laboratories) Calcd. for $\text{C}_{19}\text{H}_{27}\text{MnO}_3\text{S}$: C, 58.44; H, 6.98; Mn, 14.07; S, 8.21. Found: C, 59.00; H, 6.85; Mn, 14.00; S, 7.56.

[Au]-S(CH₂)₁₁-(η^5 -C₅H₄)Mn(CO)₃. Functionalization of Au coated Si wafer pieces was carried out by immersing the substrate in a 1 mM solution of II in hexane under Ar overnight. The derivatized pieces were rinsed with hexane upon removal from solution and characterized immediately by FT-IR.

Instrumentation. UV-vis absorption spectra were recorded on a Cary 17 UV-vis-nir spectrophotometer or on a HP 8451A diode array spectrometer. IR spectra were recorded on either a Nicolet 60SX or upgraded 7199 FT-IR. ¹H NMR spectra were recorded on a Bruker AC250 or WM250 Fourier transform spectrometer. Mass spectra were recorded on a Finnigan Mat system 8200.

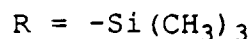
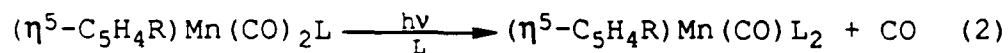
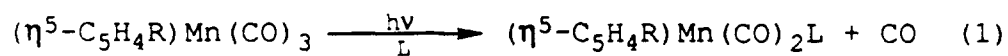
IR spectra of solution species were recorded in alkane solutions in a cell with NaCl windows. IR spectra of high surface area SiO₂-confined materials were recorded as Nujol mulls between CaF₂ plates. IR spectra of Si wafer or Au-confined species were recorded as simple transmission spectra in air with 512 scans at 2 cm⁻¹ resolution and at a gain of 4. Interferograms of the Si or Au-confined species were corrected prior to transforming in order to reduce interference patterns in the final spectra.

Irradiations. Photolysis experiments involving solution or high surface area SiO₂-confined species employed a Bausch and Lomb SP200 high-pressure Hg lamp equipped with a 10 cm H₂O filter with quartz windows. Photoreactions of Si wafer or Au-confined species were carried out with two Sylvania

blacklight bulbs with maximum output at ~355 nm. Quantum yields were measured in a merry-go-round¹² equipped with a 550 W Hanovia medium-pressure Hg lamp filtered to isolate the 366 nm Hg emission. Samples to be irradiated for quantum yield determinations were 6 mM in metal carbonyl and 60 mM in $\text{PPh}_2(n\text{-octyl})$ in methylcyclohexane. The samples were freeze-pump-thaw degassed in three cycles in 3.0 mL aliquots in ampules prepared from 13 x 100 mm Pyrex test tubes and were hermetically sealed. Ferrioxalate actinometry¹³ was used to determine light intensity, typically 1×10^{-7} einstein/min. Quantitative analyses were made by monitoring IR spectral changes.

Results and Discussion

Near-UV irradiation of a deoxygenated *n*-hexane solution containing 5 mM $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ and 50 mM $\text{L} = \text{PPh}_2(n\text{-octyl})$ at 25 °C results in the disappearance of IR bands at 2029 and 1947 cm^{-1} associated with $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, Figure 1a. Bands at 1938 and 1877 cm^{-1} assigned to the photosubstitution product $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, equation (1), appear immediately upon irradiation of the sample. A band at 1837 cm^{-1} appears upon further irradiation and is assigned to $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ formed by substitution of CO by L in $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, equation (2). Figure 1b illustrates the



formation of $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$, 1837 cm^{-1} , upon irradiation of an *n*-hexane solution containing 6 mM of pure $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, 1938, 1877 cm^{-1} , and 60 mM $\text{PPh}_2(n\text{-octyl})$. The initial quantum yields at 366 nm for the processes represented in equations (1) and (2) are 0.63 ± 0.06 and 0.25 ± 0.03 , respectively. Thus, $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ shows unexceptional photochemical behavior and yields photoproducts analogous to those formed upon irradiation of $(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ in the presence of phosphines.⁷ UV-vis and IR spectral features for relevant species are given in Table I.

Figure 2a shows the IR absorption spectrum for $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_3$ suspended in a Nujol mull containing $\sim 1.5 \text{ M L} = \text{PPh}_2(n\text{-octyl})$. From elemental analysis, the coverage of the metal carbonyl is well below monolayer. Figure 2b shows IR spectral changes accompanying the near-UV irradiation of this mixture. Bands at 2023 and 1946 cm^{-1} decline. The band at 2023 cm^{-1} is associated with $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_3$, and the band at 1946 cm^{-1} is a result of the disappearance of the 1938 cm^{-1} band of $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_3$ and the growth of the higher energy band of $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$. The actual position of the higher energy IR band of the photosubstitution product is $\sim 1931 \text{ cm}^{-1}$ and was obtained from an absorption spectrum recorded after nearly all of $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_3$ was converted to $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$. A band at 1861 cm^{-1} assigned to $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$ also appears. Apparently, $[\text{SiO}_2]\text{-O-Si(CH}_3)_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}\text{L}_2$ does not form. The IR band positions of the surface-confined materials agree fairly well with those of the related solution species, but the bands of the surface-confined species are much broader and slightly red shifted.

Irradiation of $[\text{Si}]\text{-O-Si-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_3$ in air results solely in the decline of IR bands at 2025 and 1939 cm^{-1} associated with the Si-confined I, Figure 3a. If the extinction coefficients of the solution complexes, Table I, and of the corresponding Si-confined complexes are

assumed to be the same, the coverage of the metal carbonyl can be determined from the magnitude of the negative peaks in the difference spectrum corresponding to complete photodecomposition of the surface-confined complex.

Coverage of the tricarbonyl appears to be about 2.3×10^{-10} mol/cm², or roughly one monolayer. Similar values are obtained if peak areas rather than maximum extinction coefficients are used to determine surface coverage. The coverage of redox active ferrocene by treatment of (100) Si with the derivatizing reagent (1,1'-ferrocenediyl)dimethylsilane has been shown to be $\sim 2 \times 10^{-10}$ mol/cm².¹⁴

Irradiation of [Si]-O-Si-(η^5 -C₅H₄)Mn(CO)₃ in neat, freshly distilled, deoxygenated L = PPh₂(n-octyl) results in the disappearance of IR bands at 2025 and 1939 cm⁻¹ associated with Si-confined I and the appearance of bands at 1939 and 1867 cm⁻¹ assigned to [Si]-O-Si-(η^5 -C₅H₄)Mn(CO)₂L, Figure 3b. The product band positions agree well with those of the analogous high surface area SiO₂-confined species. From the relative extinction coefficients of the solution tricarbonyl and dicarbonyl phosphine complexes, it appears that [Si]-O-Si-(η^5 -C₅H₄)Mn(CO)₂L is generated in about 75 percent yield from [Si]-O-Si-(η^5 -C₅H₄)Mn(CO)₃.

For [Si]-O-Si-(η^5 -C₅H₄)Mn(CO)₃, very high phosphine concentrations (3.3 M for neat PPh₂(n-octyl)) are required for efficient photosubstitution. For metal carbonyls in solution, entering ligand concentrations of <0.01 are often

adequate to efficiently trap coordinatively unsaturated intermediates formed by CO loss from the parent molecule. For example, near-UV irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ in hexane containing 0.01 M $\text{PPh}_2(n\text{-octyl})$ gives efficient formation of substitution products. An additional observation is that no surface-confined bisphosphine adduct $[\text{Si}]\text{-O-Si-}(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ is formed. Because the surface is close to the Mn center, formation of the bisphosphine adduct may be sterically disfavored. The need for high entering group concentrations may result from the presence of surface silanol groups capable of competing with the phosphine for reaction with the Mn center.

It was expected that $[\text{Au}]\text{-S}(\text{CH}_2)_{11}\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ would have its metal center further removed from the surface and behave more like a species in solution. Irradiation of a deoxygenated methylcyclohexane solution 1 mM in II and 0.05 M in $\text{L} = \text{PPh}_2(n\text{-octyl})$ at 25 °C results in the disappearance of II, indicated by the decline in its IR bands at 2022 and 1940 cm^{-1} and the immediate growth of bands at 1931 and 1871 cm^{-1} assigned to $\text{HS}(\text{CH}_2)_{11}\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, Figure 4. Further irradiation results in the growth of a band at 1827 cm^{-1} assigned to $\text{HS}(\text{CH}_2)_{11}\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ apparently formed from the dicarbonyl phosphine. Hence, the solution photochemistry of II parallels that of $(\text{CH}_3)_3\text{Si-}(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$.

The IR spectrum of $[\text{Au}]\text{-S}(\text{CH}_2)_{11}\text{-}(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ is shown in Figure 5a. Coverage of II is approximately

monolayer, as determined in the same manner as the coverage of metal carbonyl on Si surfaces treated with I.

Irradiation of $[\text{Au}]-\text{S}(\text{CH}_2)_{11}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ in 0.1 M L = $\text{PPh}_2(n\text{-octyl})$ in dry hexane under Ar results in the decline of IR bands at 2015 and 1925 cm^{-1} associated with Au-confined II and the growth of bands at 1922 and 1852 cm^{-1} assigned to $[\text{Au}]-\text{S}(\text{CH}_2)_{11}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, Figure 5a. Eventually, after extensive irradiation the monosubstitution product is photodegraded.

Photosubstitution reactions of $[\text{Au}]-\text{S}(\text{CH}_2)_{11}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, were successfully carried out with L = $\text{PPh}_2(n\text{-octyl})$ concentrations of 0.05 M-0.1 M. Yet, no $[\text{Au}]-\text{S}(\text{CH}_2)_{11}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$ is detected. Close packing of the metal carbonyl head groups and of the hydrocarbon chains could render the formation of the disubstitution product sterically unfavorable. Also, if close packing does exist, the metal carbonyl head group of $[\text{Au}]-\text{S}(\text{CH}_2)_{11}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$ could behave in the monolayer as it would in a solid matrix. $(\eta^5-\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{PPh}_3$ irradiated in methylcyclohexane, 3-methyl pentane, or 2-methyl THF matrices at 110K fails to undergo ligand loss (CO or PPh_3), as no IR spectral changes can be observed. In contrast, irradiation of $(\text{CH}_3)_3\text{Si}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ in a methylcyclohexane matrix induces CO loss to give the $16e^-$ species $(\text{CH}_3)_3\text{Si}-(\eta^5-\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$, analogous to results for related complexes.¹⁵ These low temperature matrix experiments suggest that dissociative CO loss from the

the monosubstituted species is less efficient for the molecule in a rigid matrix than in a fluid solution. The surface-confined monosubstituted species may behave as if it were in a rigid matrix.

Photochemical patterning of the Si and Au surfaces was accomplished by immersing ~16 mm x 32 mm pieces of Si derivatized with I and Au derivatized with II in the appropriate phosphine solutions and irradiating only one half of the surface. By IR the dicarbonyl phosphine formed only on the irradiated half, while the tricarbonyl remained on the unirradiated portion.

Conclusion

Monolayers of derivatives of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ I and II have been formed by self-assembly on the surfaces of single crystal Si and Au, respectively. The surface-confined species are readily characterized by transmission FT-IR spectroscopy.

Surface-confined I and II are photosensitive with respect to CO loss; however, CO replacement by bulky ligands is limited to a single substitution, whereas multiple substitutions occur for the molecules in solution. Steric constraints created by the Si surface or the monolayer may be responsible for the limited uptake of the entering ligand.

Si surfaces modified with I and Au surfaces modified with II can be patterned with respect to their photoproducts with $\text{PPh}_2(n\text{-octyl})$. We hope to use this technique to tailor microfabricated structures with different functional groups. Work in progress is now directed toward photochemically patterning an array of Au microwires derivatized with II.

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Table I. Spectroscopic Data for Relevant Compounds^a

Compound	IR ν_{CO} (ϵ or rel OD) ^b	UV-VIS (ϵ) ^c
$(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2029(7100), 1947(10,500)	330(940)
$(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}^d$	1938(7200), 1877(7200)	292(1960), 355(1010)
$(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$	1837	
$\text{HS}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2022(1.0), 1940(1.4)	
$\text{HS}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$	1931(1.3), 1871(1.0)	
$\text{HS}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$	1827	
$\text{CH}_3\text{OSi}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2026(1.0), 1946(1.5)	
$[\text{SiO}_2]-\text{O}-\text{Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2023(1.0), 1938(1.0)	
$[\text{SiO}_2]-\text{O}-\text{Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$	1931(1.1), 1861(1.0)	
$\text{Cl}_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2036(1.0), 1960(1.2)	
$[\text{Si}]-\text{O}-\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2025(1.0), 1939(1.2)	
$[\text{Si}]-\text{O}-\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$	1939(1.0), 1867(2.7)	
$[\text{Au}]-\text{S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2015(1.0), 1925(1.3)	
$[\text{Au}]-\text{S}(\text{CH}_2)_{11}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$	1922(1.0), 1852(1.0)	

^a All data were recorded at 298 K. All data for solution species were recorded in alkane solution. For high surface area SiO_2 supported species, IR spectra were recorded as Nujol mulls. Characteristic frequencies for Si wafer and Au supported species were obtained from transmission IR spectra.

^b Band positions in cm^{-1} . Extinction coefficients are in $\text{cm}^{-1} \text{M}^{-1}$.

^c Band positions in nm. Extinction coefficients are in $\text{cm}^{-1} \text{M}^{-1}$.

^d L = $\text{PPh}_2(n\text{-octyl})$

Figure Captions

Figure 1. (A) IR difference spectra accompanying photoreaction of $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, 2029, 1947 cm^{-1} , with $\text{L} = \text{PPh}_2(n\text{-octyl})$ in n -hexane at 25 °C to give $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, 1938, 1877 cm^{-1} , and $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$, 1837 cm^{-1} . (B) IR difference spectra accompanying photoreaction of $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, 1938, 1877 cm^{-1} , with $\text{L} = \text{PPh}_2(n\text{-octyl})$ in n -hexane at 25 °C to give $(\text{CH}_3)_3\text{Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})\text{L}_2$, 1837 cm^{-1} .

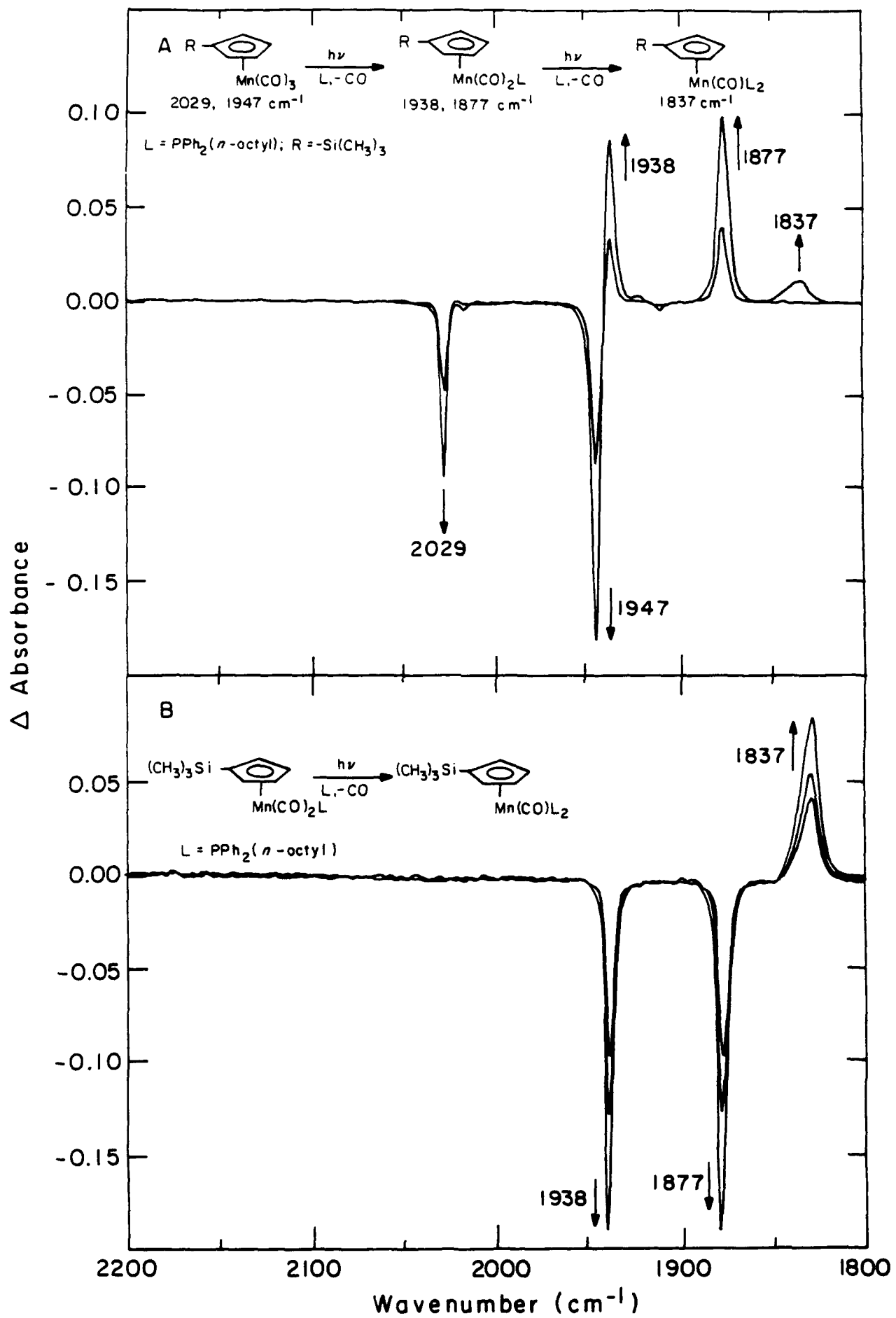
Figure 2. (A) IR spectrum of $[\text{SiO}_2]\text{-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, 2023, 1938 cm^{-1} , in a Nujol mull at 25 °C. (B) IR spectral changes accompanying photoreaction of $[\text{SiO}_2]\text{-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ with $\text{L} = \text{PPh}_2(n\text{-octyl})$ at 25 °C to give $[\text{SiO}_2]\text{-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$. Bands at 2023 and 1861 cm^{-1} are assigned to $[\text{SiO}_2]\text{-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ and $[\text{SiO}_2]\text{-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, respectively. The band at 1946 cm^{-1} is a result of the disappearance of starting material and the formation of $[\text{SiO}_2]\text{-Si}(\text{CH}_3)_2-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$.

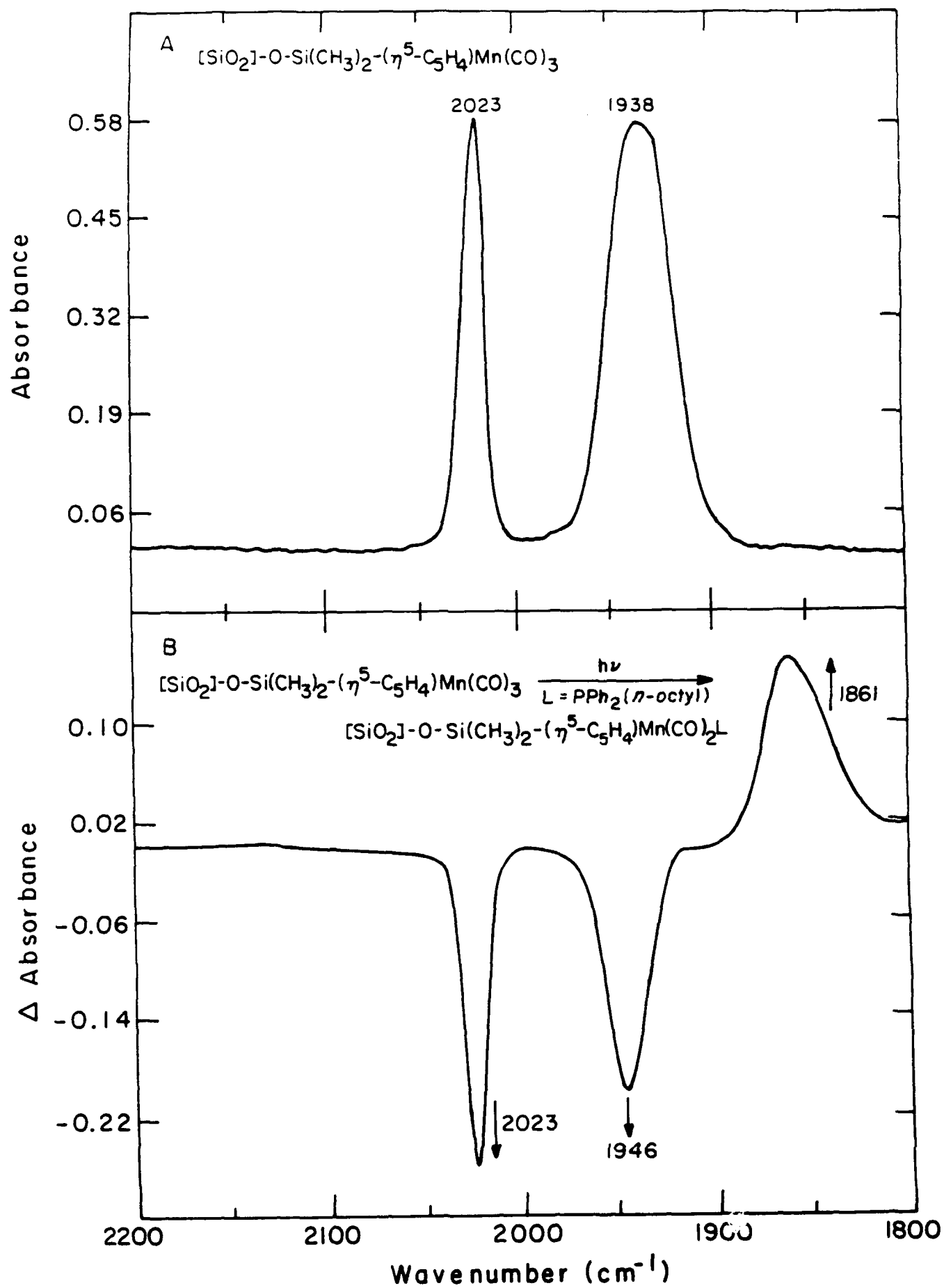
Figure 3. (A) IR difference spectrum accompanying photodecomposition of $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, 2025, 1939 cm^{-1} , upon irradiation in air at 25 °C (B) IR difference spectrum accompanying photoreaction of $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ with $\text{L} = \text{PPh}_2(n\text{-octyl})$ at 25 °C to give $[\text{Si}]\text{-O-Si}-(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$.

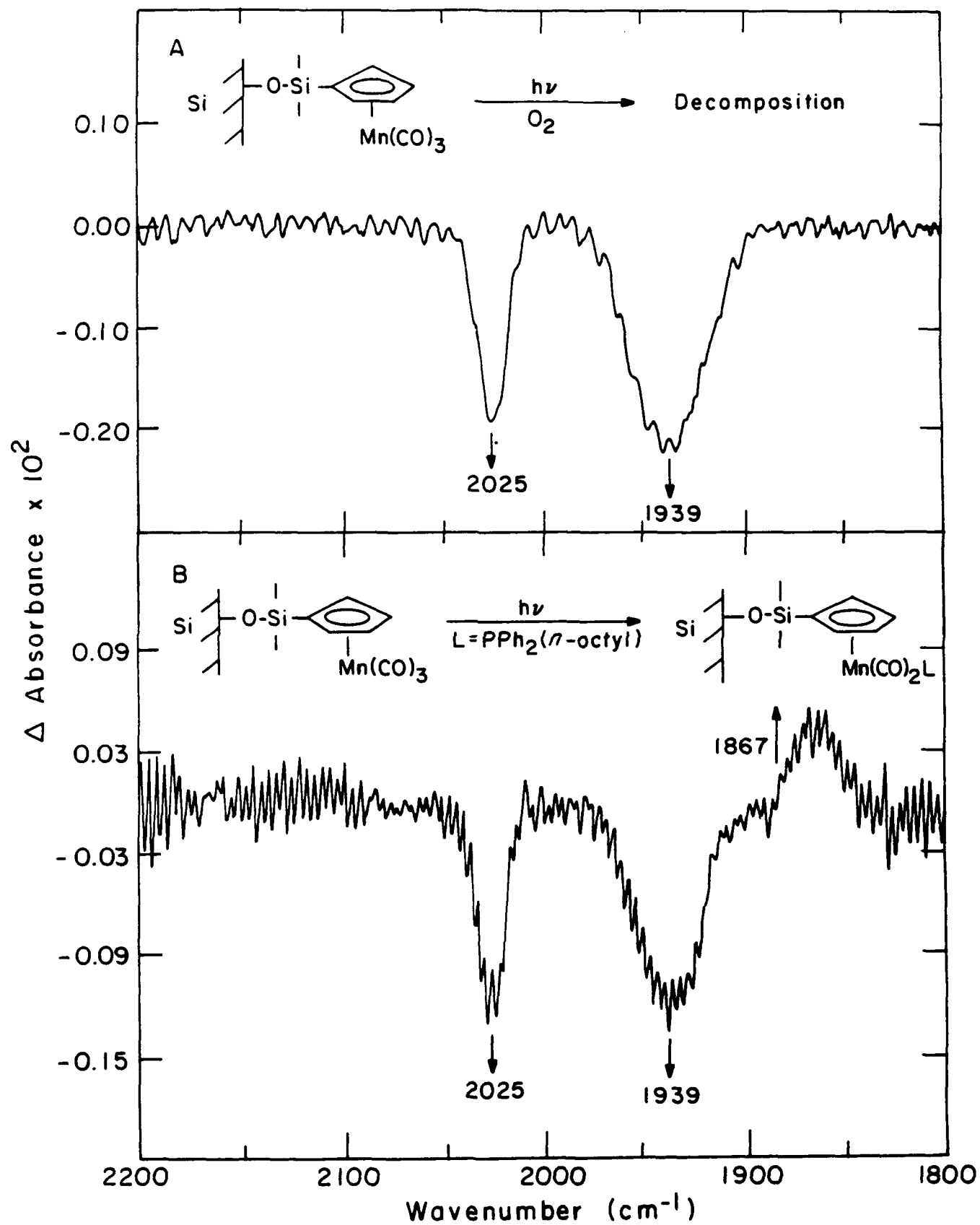
$\text{C}_5\text{H}_4\text{Mn(CO)}_3$ at 25 °C in the presence of $\text{L} = \text{PPh}_2(n\text{-octyl})$ to give $[\text{Si}]\text{-O-Si-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$, 1939, 1867 cm^{-1} .

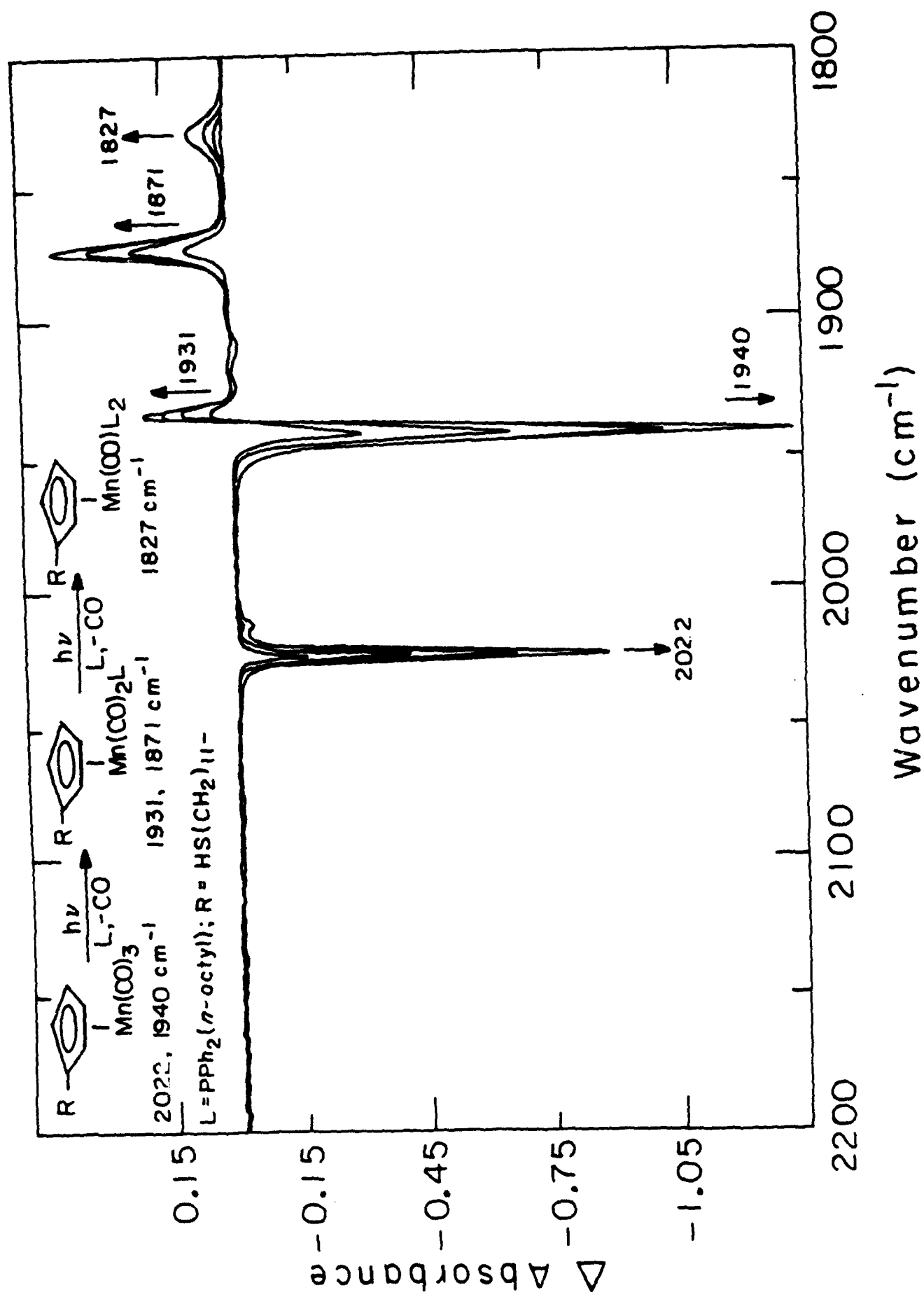
Figure 4. IR difference spectrum accompanying photoreaction of $\text{HS(CH}_2\text{)}_{11}\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_3$, 2022, 1940 cm^{-1} , with $\text{L} = \text{PPh}_2(n\text{-octyl})$ in methylcyclohexane at 25 °C to give $\text{HS(CH}_2\text{)}_{11}\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$, 1931, 1871 cm^{-1} , and $\text{HS(CH}_2\text{)}_{11}\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO) L}_2$, 1827 cm^{-1} .

Figure 5. (A) Initial IR spectrum (1) of $[\text{Au}]\text{-S(CH}_2\text{)}_{11}\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_3$, 2015, 1925 cm^{-1} , at 25 °C in the air and final IR spectrum (2) after photoreaction with $\text{L} = \text{PPh}_2(n\text{-octyl})$ to give $[\text{Au}]\text{-S(CH}_2\text{)}_{11}\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)Mn(CO)}_2\text{L}$, 1922, 1852 cm^{-1} .
(B) Difference IR spectrum of (1) and (2).

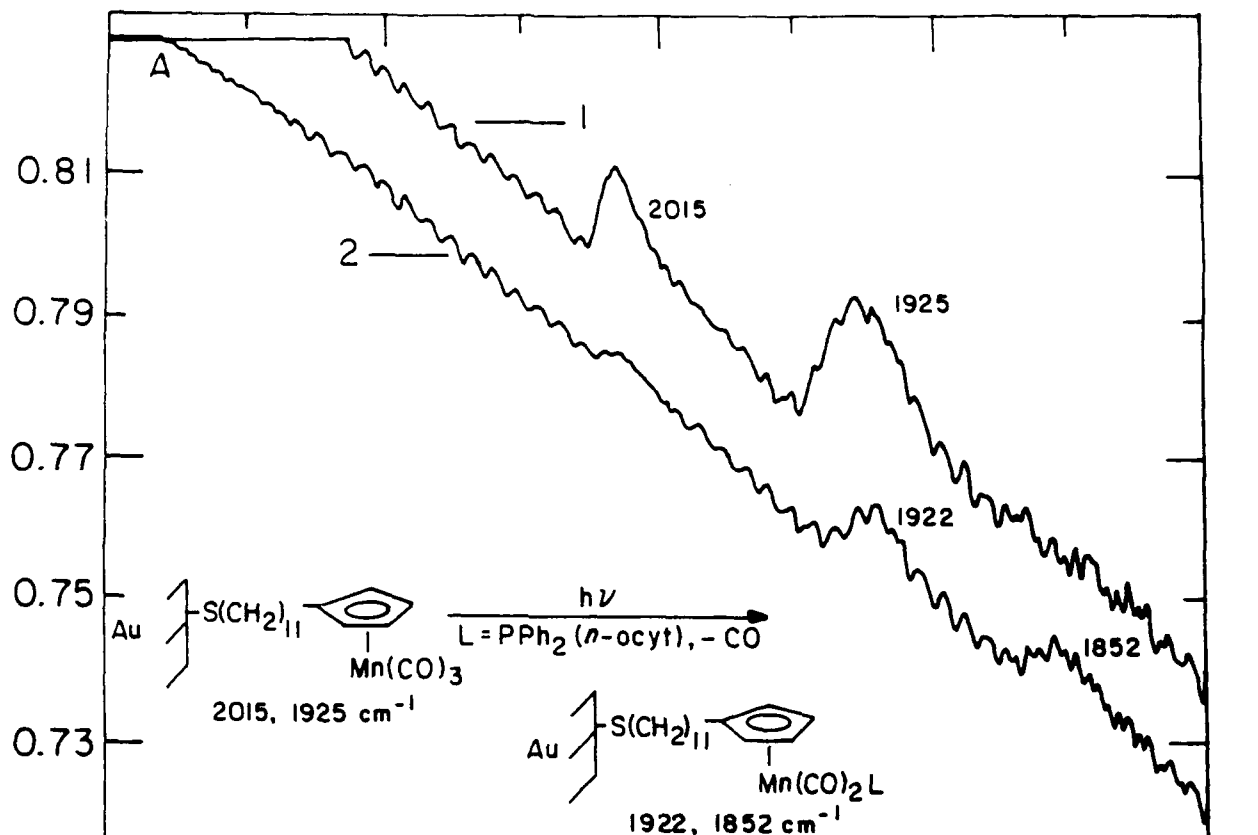
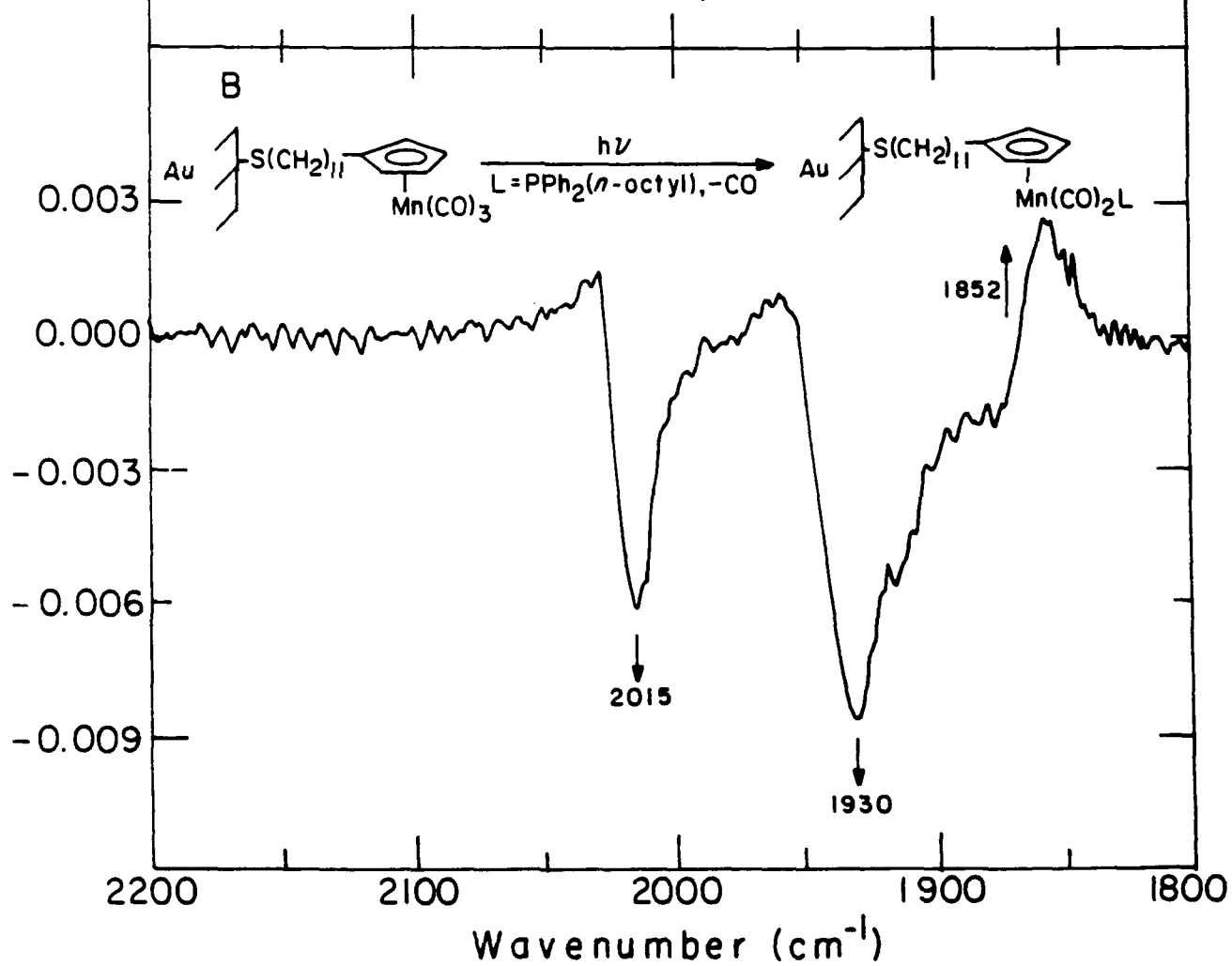








Absorbance

 Δ Absorbance

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